CLAIMS

What is claimed is:

1. A monomer having the following structure:

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wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine; and

n is 1 or 2.

2. The monomer of claim 1 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r=1 to 20, $(CF_2CF_2)_rOCF_2CF_2$ wherein r=0 to 6, and $CF(CF_3)O)_rCF_2CF_2$ wherein r=1 to 8.

3. The monomer of claim 2 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 2.

4. The monomer of claim 1 wherein n is 1.

5. A homopolymer having the following structure:

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wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2.

6. The homopolymer of claim 5 wherein R_F is selected from the group consisting of (CF₂)_r wherein r = 1 to 20, (CF₂CF₂)_rOCF₂CF₂ wherein r = 0 to 6, and CF(CF₃)O)_rCF₂CF₂ wherein r = 1 to 8.

7. The homopolymer of claim 6 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 2.

- 8. The homopolymer of claim 1 wherein n is 1.
- 9. A copolymer selected from the group consisting of: (a) a copolymer having the structure:

$$\begin{pmatrix}
CF-CF_2 \\
(R_FSO_2F)_n
\end{pmatrix}_{X}
\begin{pmatrix}
CF-CF_2 \\
Y
\end{pmatrix}_{m}$$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or l; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

15 n is 1 or 2.

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m and x are mole fractions wherein m is 0.01 to 0.99 and x is 0.99 to 0.01; and

x+m=1

(b) a copolymer having the structure:

 $\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{Y}
\end{pmatrix}
\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{R_FSO_2F}
\end{pmatrix}_{\mathsf{n}}
\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{CF-CF_2}
\end{pmatrix}_{\mathsf{Z}}$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01, and

z is 0.0001 to 0.10

m + x + z = 1.

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10. The copolymer of claim 9 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 20, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 6, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 8.

- 11. The copolymer of claim 10 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 2.
- 12. The copolymer of claim 9 wherein the linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms is selected from the group consisting of C_nF_{2n+1} , wherein n is 1 to 10; and C_nH_{2n+1} , wherein n is 1 to 10.c
- 13. The copolymer of claim 9 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms is selected from the group consisting of $CF_3(CF_2)_qO(CF_2CF_2)_q$ wherein q=1 to 5 and $CF_3CF_2CF_2(OCFCF_3)_q$ wherein q=1 to 5.
- 14. The copolymer of claim 13 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine is selected from the group consisting of $CF_3(CF_2)_qOCF_2CF_2$ wherein q = 1 to 2, and $CF_3CF_2CF_2(OCFCF_3)_q$ wherein q = 1 to 3.
 - 15. The copolymer of claim 14 wherein n is 1.
- 16. The copolymer of claim 9 wherein m and x are mole fractions, wherein m is 0.1 to 0.4; and x is 0.9 to 0.6 in structure $\bf 3$.
- 17. The copolymer of claim 9 wherein m, x and z are mole fractions, wherein m is 0.2 to 0.6; x is 0.4 to 0.8; and z is 0.002 to 0.01 in structure 4.
- 18.A polymer electrolyte membrane prepared from a homopolymer or copolymer selected from the group consisting of:
 - (a) a homopolymer having the structure:

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2;

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(b) a copolymer having the structure:

$$\begin{pmatrix}
\mathsf{CF-CF_2} \\
(\mathsf{R_FSO_2F})_{\mathsf{n}}
\end{pmatrix}_{\mathsf{x}}
\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{Y}
\end{pmatrix}_{\mathsf{m}}$$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

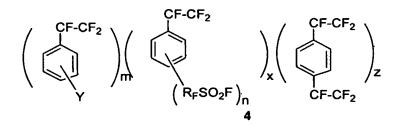
Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2,

m and x are mole fractio wherein m is 0.01 to 0.99 and x is 0.99 to 0.01; and

x+m = 1; and

(c) a copolymer having the structure:



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wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

m, x and z are mole fraction wherein m is 0.01 to 0.99, x is 0.99 to 0.01, and z is 0.0001 to 0.10 m + x + z = 1; and mixtures thereof.

19. The polymer electrolyte membrane of claim 18 further

comprising a porous support.

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20. The polymer electrolyte membrane of claim 18 wherein R_F in structure **2** is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 20, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 6, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 8.

21. The polymer electrolyte membrane of claim 20 wherein R_F in structure 2 is selected from the group consisting of $(CF_2)_r$ wherein r=1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r=0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r=1 to 2.

22. The polymer electrolyte membrane of claim 18 wherein, in structure 2, n is 1.

23. The polymer electrolyte membrane of claim 18 wherein R_F , in structures 3 and 4, is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 20, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 6, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 8.

24. The polymer electrolyte membrane of claim 23 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 2.

25. The polymer electrolyte membrane of claim 18 wherein the linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms, in structures 3 and 4, is selected from the group consisting of C_nF_{2n+1} , wherein n is 1 to 10; and C_nH_{2n+1} , wherein n is 1 to 10.

26. The polymer electrolyte membrane of claim 18 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms, in structures 3 and 4, is selected from the group consisting of $CF_3(CF_2)_qO(CF_2CF_2)_q$ wherein q = 1 to 5 and $CF_3CF_2CF_2(OCFCF_3)_q$ wherein q = 1 to 5.

27. The polymer electrolyte membrane of claim 26 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine is selected

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from the group consisting of $CF_3(CF_2)_qOCF_2CF_2$ wherein q = 1 to 2, and $CF_3CF_2CF_2(OCFCF_3)_q$ wherein q = 1 to 3.

- 28. The polymer electrolyte membrane of claim 18 wherein n, in structures 3 and 4, is 1.
- 29. The polymer electrolyte membrane of claim 18 wherein m and x are mole fractions, wherein m is 0.1 to 0.4; and x is 0.9 to 0.6 in structure $\bf 3$.
- 30. The polymer electrolyte membrane of claim 18 wherein m, x and z are mole fractions, wherein m is 0.2 to 0.6; x is 0.4 to 0.8; and z is 0.002 to 0.01 in structure $\bf 4$.
- 31.A polymer electrolyte membrane selected from the group consisting of:
 - (a) a membrane having the chemical structure:

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wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

(b) a membrane having the chemical structure:

(R_FSO₂Q)

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wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon

atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

Q = OM, OH, NHSO2R_F, wherein M = Li⁺, Na⁺, K⁺ or Cs⁺, n is 1 or 2.

m and x are mole fractions wherein m is 0 to 0.99,

x is 1 to 0.001, and

x + m = 1; and

(c) a membrane having the chemical structure:

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$$\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{FSO_2Q}
\end{pmatrix}_{n}$$

$$\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{CF-CF_2}
\end{pmatrix}_{z}$$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as CI, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

Q = OM, OH, NHSO2R_F, wherein M = Li⁺, Na⁺, K⁺ or Cs⁺, n is 1 or 2,

m, x and z are mole fractions wherein m is 0.01 to 0.99, x is 0.99 to 0.01,

z is 0.0001 to 0.10, and

m + x + z = 1

32. A membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, wherein the membrane is prepared from a homopolymer or copolymer selected from the group consisting of:

(a) a homopolymer having the structure:

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wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2;

(b) a copolymer having the structure:

$$\begin{pmatrix}
\mathsf{CF-CF_2} \\
(\mathsf{R_FSO_2F})_n
\end{pmatrix}_{\mathsf{x}}
\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{Y}
\end{pmatrix}_{\mathsf{m}}$$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2.

m and x are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01; and

x+m = 1; and

(c) a copolymer having the structure:

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$$\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{F-CF_2}
\end{pmatrix}_{\mathsf{m}}
\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{R_FSO_2F}
\end{pmatrix}_{\mathsf{n}}
\begin{pmatrix}
\mathsf{CF-CF_2} \\
\mathsf{CF-CF_2}
\end{pmatrix}_{\mathsf{Z}}$$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2.

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m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01, and

z is 0.0001 to 0.10

m + x + z = 1; and mixtures thereof.

- 33. The membrane electrode assembly of claim 32 wherein the polymer electrolyte membrane further comprises a porous support.
- 34. The membrane electrode assembly of claim 32 further comprising at least one electrode prepared from an electrocatalyst coating composition present on the first and second surfaces of the membrane.
- 35. The membrane electrode assembly of claim 34 further comprising at least one gas diffusion backing present on the at least one electrode on the side away from the polymer electrolyte membrane.
- 36. The membrane electrode assembly of claim 32 further comprising a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.
- 37.The membrane electrode assembly of claim 32 wherein R_F in structure **2** is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 20, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 6, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 8.
- 38. The membrane electrode assembly of claim 37 wherein R_F in structure 2 is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 2.
- 39. The membrane electrode assembly of claim 32 wherein n, in structure 2, is 1.
- 40. The membrane electrode assembly of claim 32 wherein R_F , in structures **3** and **4**, is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 20, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 6, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 8.

41. The membrane electrode assembly of claim 40 wherein R_F is selected from the group consisting of $(CF_2)_r$ wherein r = 1 to 8, $(CF_2CF_2)_rOCF_2CF_2$ wherein r = 0 to 2, and $CF(CF_3)O)_rCF_2CF_2$ wherein r = 1 to 2.

42. The membrane electrode assembly of claim 32 wherein the linear or branched perfluoroalkyl and non-fluorinated alkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms, in structures 3 and 4, is selected from the group consisting of C_nF_{2n+1} , wherein n is 1 to 10; and C_nH_{2n+1} , wherein n is 1 to 10.

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- 43. The membrane electrode assembly of claim 32 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms, in structures 3 and 4, is selected from the group consisting of $CF_3(CF_2)_qO(CF_2CF_2)_q$ wherein q = 1 to 5 and $CF_3CF_2CF_2(OCFCF_3)_q$ wherein q = 1 to 5.
- 44. The membrane electrode assembly of claim 43 wherein the perfluoroalkyl group containing oxygen, chlorine or bromine is selected from the group consisting of $CF_3(CF_2)_qOCF_2CF_2$ wherein q = 1 to 2, and $CF_3CF_2CF_2(OCFCF_3)_q$ wherein q = 1 to 3.
- 45. The membrane electrode assembly of claim 32 wherein n, in structures 3 and 4, is 1.
 - 46. The membrane electrode assembly of claim 32 wherein m and x are mole fractions, wherein m is 0.1 to 0.4; and x is 0.9 to 0.6 in structure $\bf 3$.
- 47. The polymer electrolyte membrane of claim 46 wherein m, x and z are mole fractions, wherein m is 0.2 to 0.6; x is 0.4 to 0.8; and z is 0.002 to 0.01 in structure 4.
- 48. A electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the membrane is prepared from a homopolymer or copolymer selected from the group consisting of:
 - (a) a homopolymer having the structure:

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

n is 1 or 2;

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(b) a copolymer having the structure:

$$\left(\begin{array}{c} CF-CF_2 \\ (R_FSO_2F)_n \end{array}\right)_X \left(\begin{array}{c} CF-CF_2 \\ \end{array}\right)_m$$

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2.

m and x are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01,

x+m = 1, and

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(c) a copolymer having the structure:

wherein R_F is linear or branched perfluoroalkene group, optionally containing oxygen or chlorine,

Y is H; halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon

atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the alkyl group comprises C1 to C10 carbon atoms,

n is 1 or 2.

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m, x and z are mole fractions wherein m is 0.01 to 0.99,

x is 0.99 to 0.01,

z is 0.0001 to 0.10, and

m + x + z = 1; and mixtures thereof.

- 49. The electrochemical cell of claim 48 wherein the electrochemical cell is a fuel cell.
 - 50. The fuel cell of claim 49 wherein the polymer electrolyte membrane further comprises a porous support.
 - 51. The fuel cell of claim 49 further comprising at least one electrode prepared from an electrocatalyst containing composition present on the first and second surfaces of the polymer electrolyte membrane.
 - 52. The fuel cell of claim 51 further comprising at least one gas diffusion backing.
 - 53. The fuel cell of claim 49 further comprising a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.
 - 54. The fuel cell of claim 51 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.
 - 55. The fuel cell of claim 53 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.
 - 56. The fuel cell of claim 49 wherein the fuel is an alcohol or ether.
 - 57. The fuel cell of claim 56 wherein the fuel is methanol.
 - 58. The fuel cell of claim 49 wherein the fuel is hydrogen.

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